CHAPTER II

Standard electrode potentials of alpha and gamma manganese and the cathode potentials during electro-deposition of the same

The standard electrode potentials of alpha and gamma manganese have been determined and the values are compared with the values obtained from thermal data. It is shown that in the same group in the periodic table the standard potential values become more positive while the Gibb's free energy values become more negative. The cathode potential values during deposition of alpha and gamma manganese have been measured and related to the standard potentials. Cathode potential for the same current density increases in the order: gamma, alpha manganese containing sulphur and alpha manganese containing selenium which is found in conformity with the order of standard potential values found in this investigation.

Introduction

The standard potential values for manganese metal quoted in literatures vary widely as can be seen from Table 2.I.

TABLE 2.I – STANDARD POTENTIAL VALUES OF MANGANESE

Value calculated from thermal data by Latimer[1], Campbell[2], Conway[3], and Kubaschewski[4]	Value directly determined by Royce and Kahlenberg[5] and corrected for activity coefficient by Allan Walkley[6] *Metals handbook*[7]	Value calculated by Allan Walkley[6] from thermal data Parsons[8] Potter	Direct determination Garkavi[9]
−1·05	−1·1345	−1·182 −1·190 (corrected)	−1·06

Because of the high reactivity of manganese metal, the direct determination of the standard potential of manganese is rather difficult. And, as pointed out by Allan Walkley[6], there does not appear to have been many attempts at it other than Royce and Kahlenberg's[5] and Garkavi's[9] investigations. Taking into account the activity co-efficient of $MnCl_2$, Walkley suggests that the value of Royce proves to be −1·136 V, though the value he found, calculated from the free energy of formation of manganese ions, to be $-1{\cdot}182 \pm 0{\cdot}012$ V and later[6] corrected to −1·190. He continues to say that the standard potentials of aluminium and magnesium obtained from cell measurements are less negative than those calculated from thermal data and manganese, with its similar tendency towards film formation, may be expected to behave similarly. Further, he had used electrolytic alpha manganese, containing sulphur, for the heat of solution of manganese in HCl.

As is well known $-zFE°$ (where z is the valence of the metal M, F is the Faraday, and E° is the standard potential of M) is called the standard free energy of the formation of the M^{z+} ions, although it is really the increase in the free energy of the reaction.

$$M + zH^+(aH^+ = 1) = M^{z+}(aM^+) + \tfrac{1}{2}zH_2(1\ \text{atm})$$

with all the substances in their standard states[10].

The values for the free energy of formation of manganous ions as found by various investigators[1,2,6] vary around −48·6 and −54·89 kcal

with the calculated standard potential values varying around —1·05 and —1·10 V.

It is intended in this work to determine experimentally the standard electrode potentials of pure alpha manganese (containing no sulphur or selenium), pure gamma manganese, alpha manganese containing sulphur and alpha manganese containing selenium, and to compare with the values obtained from thermal data. The cathode potentials during actual deposition of alpha and gamma manganese have also been determined.

Materials and methods

The gamma manganese used for this investigation was prepared by electro-deposition from extremely pure solution of manganese sulphate (65 gm/l) and ammonium sulphate (135 gm/l) without any addition agent in a double compartment cell between stainless steel cathode and lead silver alloy anodes at a cathodic current density of 4·2 amp/sq dm, and a cathodic pH of 7·3 and a temperature of 28°C. The gamma manganese contained only about 42 cc of hydrogen per 100 gm of metal and no other significant impurities.

Pure alpha manganese, containing no sulphur or selenium, was prepared from a part of the above electro-deposited gamma manganese after heating at 160°C for one hour in a vacuum of 10^{-4} mm of Hg, whereby it was completely transformed to alpha manganese. The transformed manganese was etched for 30 seconds in 5 per cent Nital.

Alpha manganese specimens, containing sulphur and selenium, were prepared as above but from solutions containing 0·1 gm of sulphur dioxide or 0·1 gm of selenious acid per litre of electrolyte respectively. The specimens contained, respectively, 0·07 per cent sulphur and 231 cc of hydrogen per 100 gm, and 0·3 per cent selenium and 255·7 cc of hydrogen per 100 gm.

Standard potential — A normal solution of manganese sulphate was prepared by dissolving pure gamma manganese in guaranteed reagent dilute sulphuric acid. The solution was boiled with gamma manganese for half an hour, cooled, filtered and kept in a closed measuring flask. The pH of the solution was 5·5.

About 3×3 cm manganese pieces were used. In all cases the surface, which was towards the cathode side and which had a tarnish resistant brightness, was used for the determination of the standard potential, while the other side towards the solution during deposition was coated with cellulose acetate dissolved in acetone to make that side nonconducting.

Half of the surface of manganese pieces was dipped in the prepared manganese sulphate solution in a beaker and the attached copper wire was connected to one terminal of the potentiometer. A saturated potassium chloride agar bridge was used in conjunction with Beckman saturated calomel electrode which was connected to the other terminal of the potentiometer. From the moment the manganese electrode was dipped in solution, the potential readings were taken at short intervals for about 30 minutes.

No correction has been made for the activity coefficient or for the liquid junction potentials. The values were intended for a qualitative study and cannot be taken as absolute or exact.

Cathode potential measurement — The cathode potentials were measured for the first one hour under the actual running conditions. Extremely pure solutions from the same bulk were used for all determinations except that 0·1 gm of sulphur dioxide or 0·1 gm of selenious acid per litre was used for alpha depositions. Both cathode and anodes had a submerged surface area of $12{\cdot}5 \times 6$ cm. One 3 mm wide glass tube was bent at right angles at 12 cm away from each end and one end was drawn again at right angles into a tip $\frac{1}{2}$ cm long and 1 mm wide. This bent glass tube was used as a saturated potassium chloride agar bridge and was fixed such that the drawn tip was 3 mm away from the centre of the submerged surface of the cathode, while the other end was kept dipped in saturated potassium chloride solution. A saturated Beckman Calomel electrode dipped in the same potassium chloride solution was connected to the positive terminal of the Vernier potentiometer, while the cathode was connected to the negative terminal.

In each case the cell was cleaned thoroughly and fitted. The potassium chloride agar bridge was rigidly fixed 3 mm away from the centre of the cathode, the electrolyte was added and immediately the current was switched on. There was sufficient flow of electrolyte to and out of the cell and the concentration of the electrolyte in the cell was nearly kept constant. No correction was made for the ohmic resistance between the tip of glass bridge and cathode surface. As the concentration of the electrolyte was the same in all cases except for the addition of sulphur dioxide or selenious acid, the values obtained, though not absolute, have been taken as truly representative of the cathode potential values for alpha and gamma manganese deposition at the employed current density.

Results of experiments

The standard electrode potential values, with respect to saturated calomel and hydrogen electrodes as zero, of pure alpha manganese, gamma

manganese and alpha manganese containing sulphur or selenium, are given in Table 2. II.

TABLE 2.II — STANDARD ELECTRODE POTENTIAL VALUES

Nature of manganese metal	Potential values at 27°C in volts referred to saturated calomel as zero			Referred to hydrogen electrode as zero
	Extrapolated values to zero time	At or about 150 sec	At or beyond 30 min	Extrapolated value to zero time
Pure alpha manganese (transformed gamma)	−1·298	−1·276	−1·235	−1·058
Pure gamma manganese (electro-deposited)	−1·325	−1·312	−1·273	−1·085
Electro-deposited alpha manganese containing sulphur	−1·332	−1·325	−1·272	−1·092
Electro-deposited alpha manganese containing selenium	−1·365	−1·360	−1·342	−1·125

The change of electrode potential with time of two different specimens of each has been plotted in Figs. 2.I, 2.II, 2.III and 2.IV.

The recorded cathode potential values at constant cathodic current density, during actual deposition of gamma manganese from pure solutions and alpha manganese from solutions containing sulphur or selenium, have been presented in Table 2.III.

Discussion

The standard potential values of alpha and gamma manganese should be, respectively, the increase in the free energy of the reactions.

$$Mn(\alpha) + 2H^+ = Mn^{2+} + H_2$$
$$Mn(\Upsilon) + 2H^+ = Mn^{2+} + H_2$$

with all the substances in their standard states.

For a qualitative study of the difference in standard potential of alpha and gamma manganese it can rather be presumed that the difference in standard potentials of these two modifications of manganese should depend on the standard free energy of alpha and gamma manganese at room temperature.

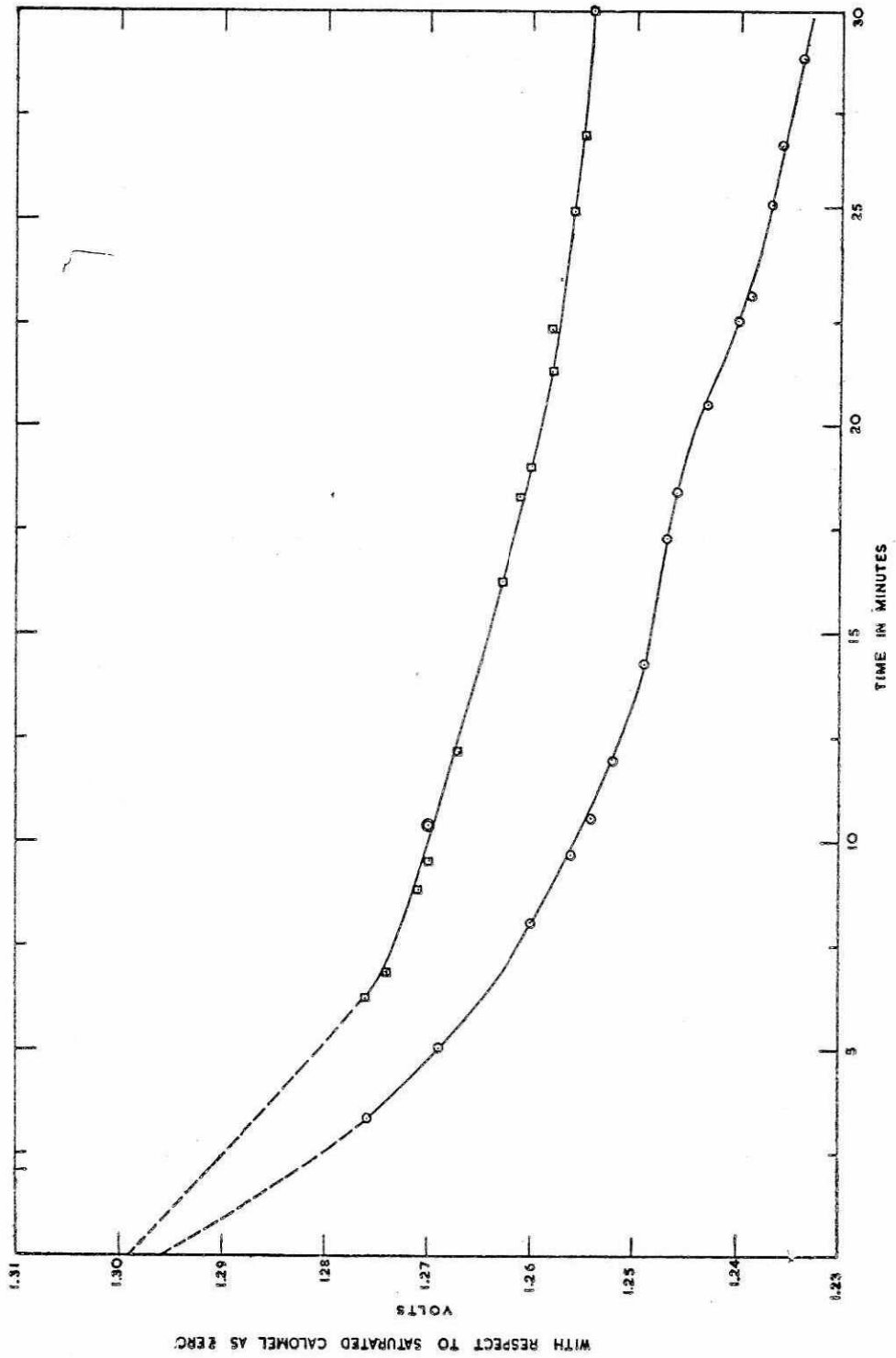

FIG. 2.1.—ELECTRODE POTENTIAL CURVE WITH TIME OF TWO DIFFERENT SAMPLES OF PURE ALPHA MANGANESE

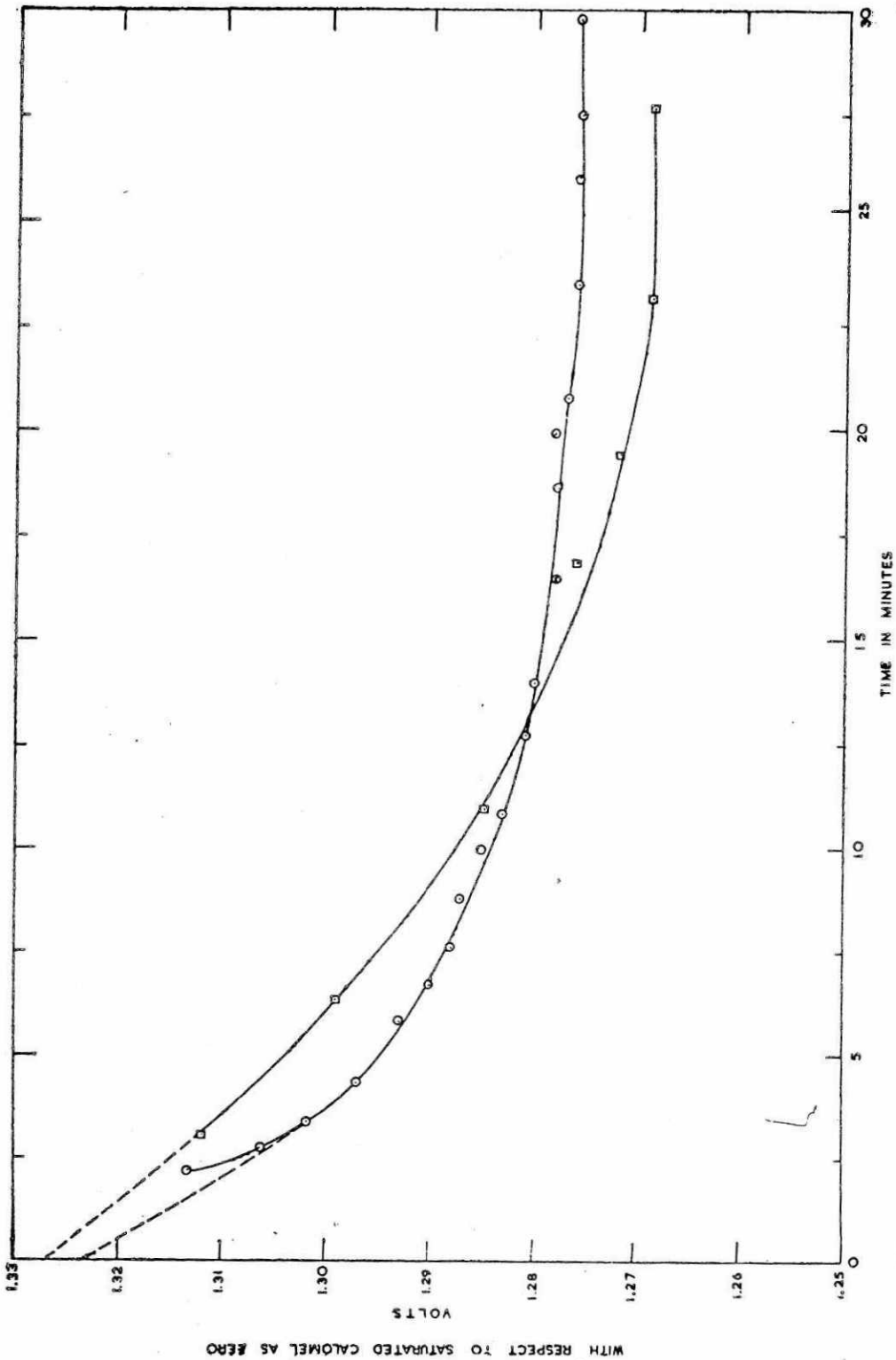

FIG. 2.II — ELECTRODE POTENTIAL CURVE WITH TIME OF TWO DIFFERENT SAMPLES OF PURE GAMMA MANGANESE

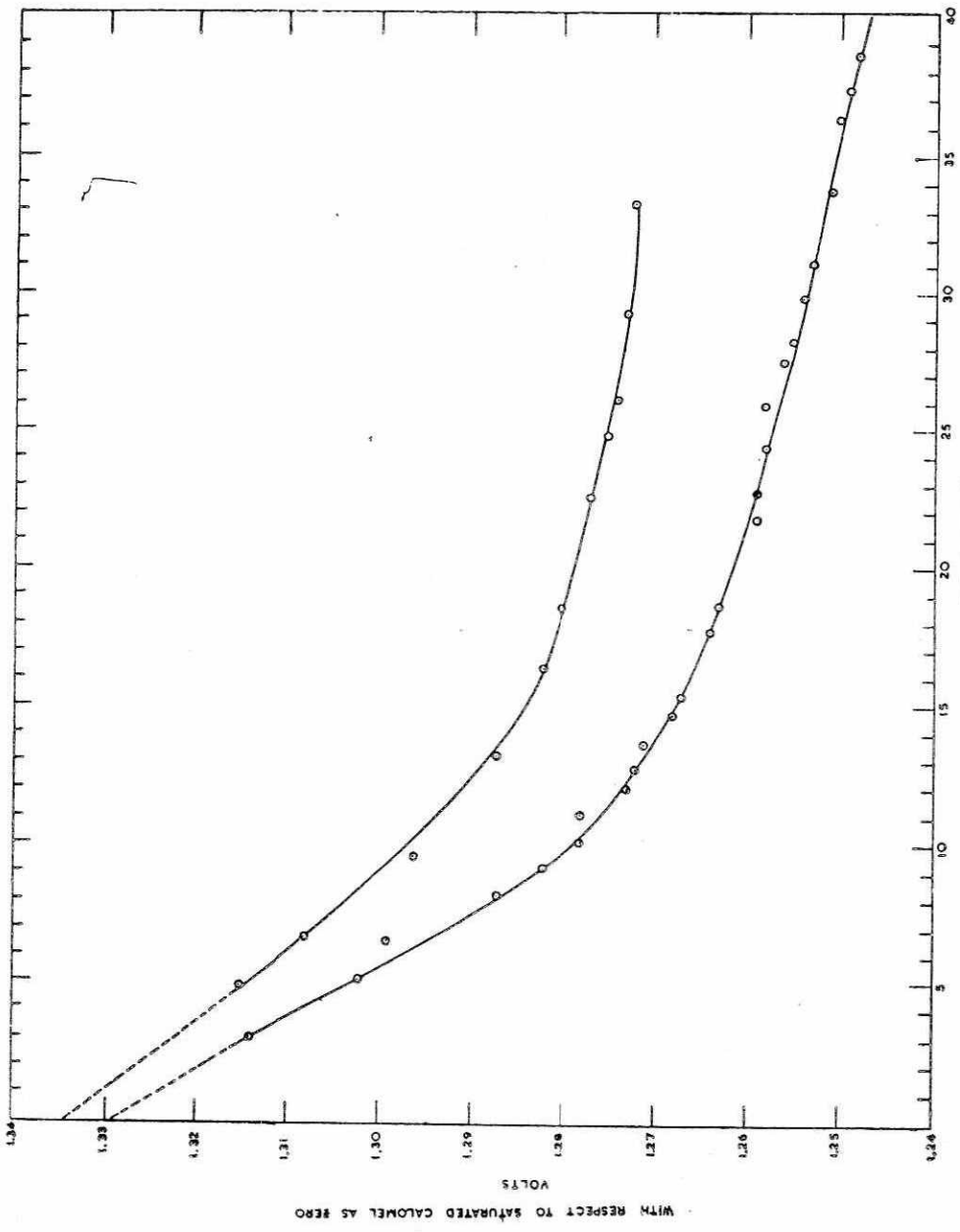

FIG. 2.III — ELECTRODE POTENTIAL CURVE WITH TIME OF TWO DIFFERENT SAMPLES OF ALPHA MANGANESE CONTAINING SULPHUR

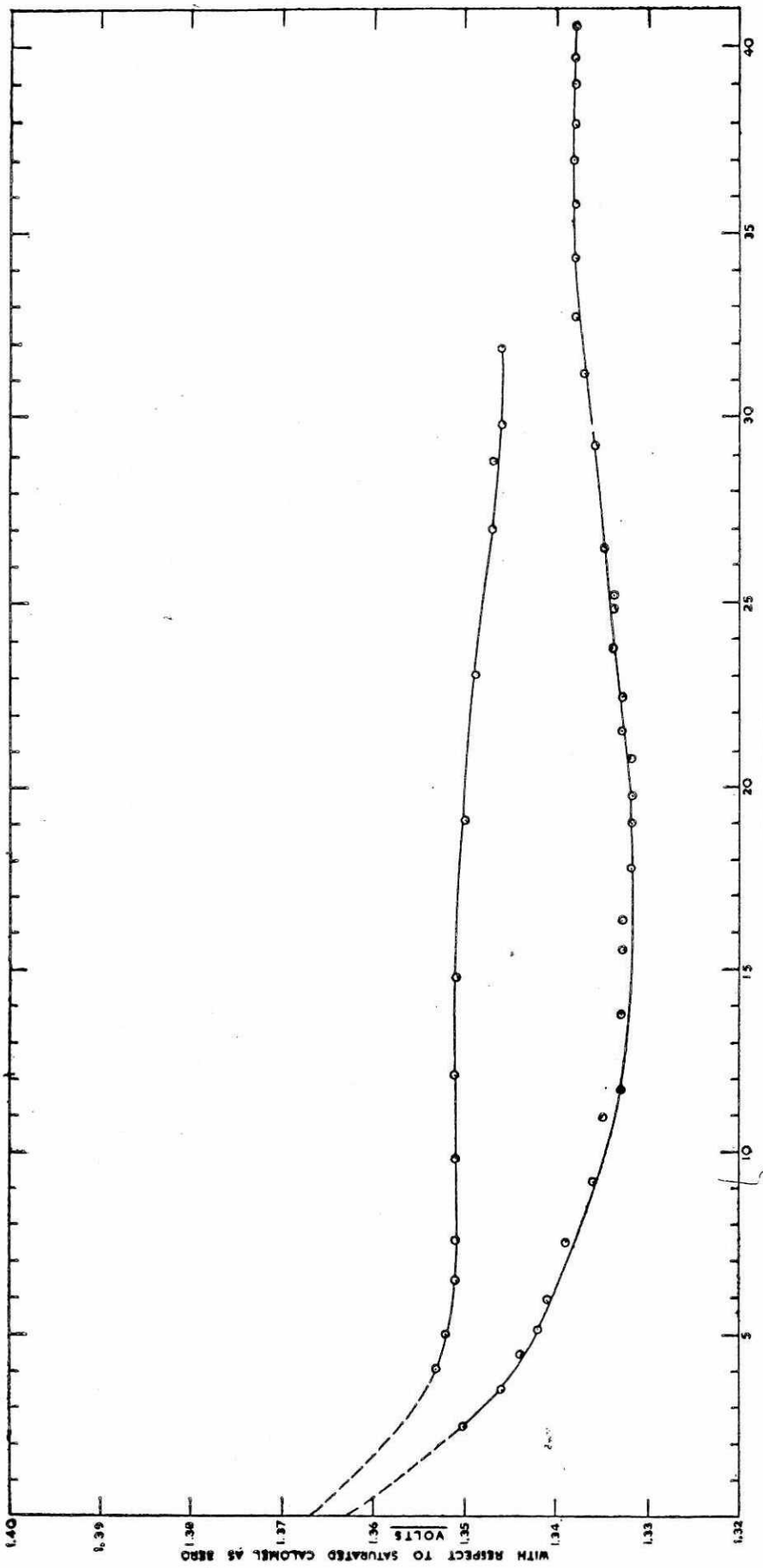

FIG. 2.IV — ELECTRODE POTENTIAL CURVE WITH TIME OF TWO DIFFERENT SAMPLES OF ALPHA MANGANESE CONTAINING SELENIUM

TABLE 2.III — CATHODE POTENTIAL VALUES DURING DEPOSITION OF ALPHA AND GAMMA MANGANESE

Conditions of deposition:

Composition per litre of electrolyte: 65 gm of manganese sulphate
135 gm of ammonium sulphate
(0·1 gm per litre of SO_2 or H_2SeO_3 for alpha deposition)
Initial pH of feed electrolyte and cell solution = 7·3
Cathodic current density = 4·2 amps per sq dm
Temperature of electrolysis = 28°C
Flow of electrolyte = 10 cc per min

Nature of manganese metal deposited	Potential values in volts referred to saturated calomel as zero	Potential values in volts referred to hydrogen electrode as zero
Gamma manganese	−1·631	−1·392
Alpha manganese containing sulphur	−1·638	−1·399
Alpha manganese containing selenium	−1 647	−1·408

Calculating from data on specific heat and heat content of various phases of manganese, Christian[11] has shown that the difference in free energy between alpha, beta and gamma phases are everywhere very small from 0° to 1400°K. The values of specific heat, as found out by various investigators, do not differ widely and the free energy values are not significantly affected. The values, as computed by Christian, are given in Table 2.IV.

TABLE 2.IV—GIBB'S FREE ENERGY (F=H−TS) OF α, β AND γ MANGANESE[11]

Temperature °K	F_α Cal/g atom	F_β Cal/g atom	F_γ Cal/g atom
0	0	—	+342
298·16	−1070	−961	−739

Taking the free energy of the other constituents to be the same in the above two reactions, it is evident that at room temperature the

potential of gamma manganese should be more negative than that of alpha at least by

$$\frac{[-1070-(-739)]\times 4\cdot 183}{2\times 96500}$$

ie,
$$\frac{-331\times 4\cdot 183}{2\times 96500} = -0\cdot 0072 \text{ volts}$$

However, these values are not to be considered as exact and absolute. It has been referred to bring out the very small difference and the compatibility between the experimentally determined values and the calculated values as to the more negativity of the standard potential value of gamma manganese.

In Table 2.V and Figs. 2.V and 2.VI the Gibb's free energy values, as calculated from the formula $G = (H_{S_t}-H_o)-TS_{S_t}$, and the standard potential values of the elements are given. It may be noticed that in the same group the standard potential value becomes more positive while the free energy value becomes more negative. It is interesting to note that the break in the properties occurs at chromium, molybdenum and tungsten in the three long periods.

From Table 2.II and Figs. 2.I and 2.II it is seen that the standard potential value of pure alpha manganese is less negative than that of gamma manganese and that the values for the two phases differ only very slightly which is in close agreement with the standard free energy of each modification. That means, from an extremely pure solution of manganese and ammonium sulphate, apart from other interfering factors, alpha manganese, stable at room temperature, should be preferentially and initially deposited than gamma manganese.

It is interesting to note from Figs. 2.I to 2.IV that the extrapolated values of electrode potential to zero time of the two different samples of each of the specimens are in very close ranges. During the determination of these standard potential values, in all cases, within a few seconds of dipping the manganese electrode in manganese sulphate solution, the hydrogen bubbles were found sticking on to the surface, the more so with pure alpha manganese and the least with manganese containing selenium. And hence, the recorded potential values with time should be related with the hydrogen over-voltage of surface. From Fig. 2.II, it is seen that pure gamma manganese gives more or less steady values after a few minutes of dipping in the solution, as compared to pure alpha manganese, which indicates that gamma manganese has a higher hydrogen over-voltage as compared to pure alpha manganese. The almost steady values obtained in the case of alpha manganese containing selenium, as seen from Fig. 2.IV, shows the very high hydrogen over-voltage of the surface

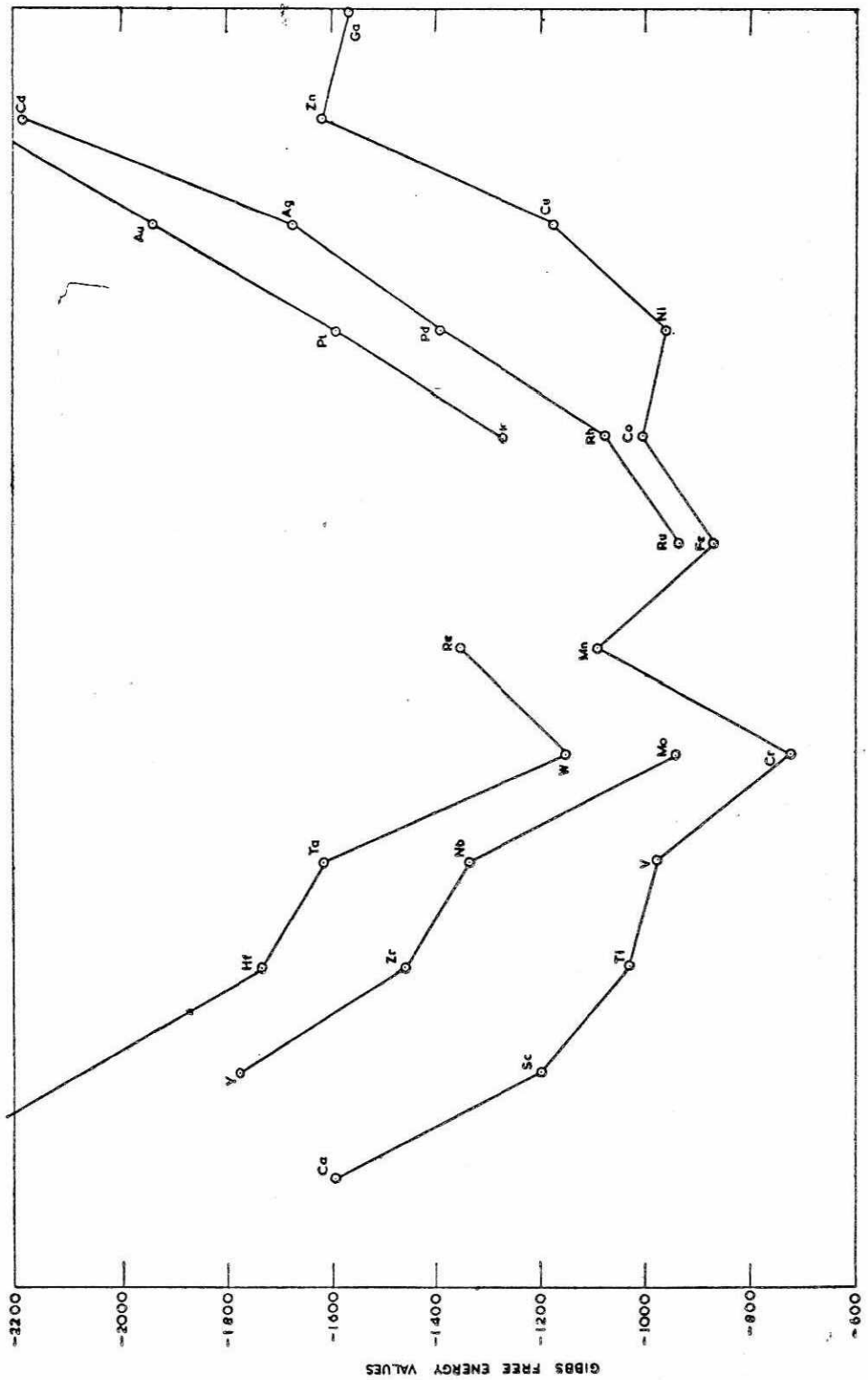

FIG. 2.V — GIBB'S FREE ENERGY VALUES OF THE ELEMENTS OF THE THREE LONG PERIODS

TABLE 2.V – STANDARD POTENTIAL VALUES AND GIBB'S FREE ENERGY VALUES OF ELEMENTS[*1,3,8,12,13]

He	Li	Be	B										C	N	O	F
	−3·01	−1·7	−0·73											−3·09		+2·85
(7501)	(934)	(212)	(125)										(157)	$\frac{(11578)}{2}$	$\frac{(12535)}{2}$	$\frac{(12330)}{2}$
Ne	Na	Mg	Al										Si	P	S	Cl
	−2·714	−2·38	−1·66										−0·86		−0·51	+1·358
(8939)	(2089)	(1134)	(924)										(582)		(1215)	$\frac{(13696)}{2}$
A	K	Ca	Sc	Ti^{2+}	V^{2+}	Cr^{3+}	Mn	Fe^{2+}	Co	Ni	Cu^{2+}	Zn	Ga^{2+}	Ge	As	Se	Br
	−2·92	−2·84	−2·08	−1·75	−1·5	−0·71	−1·05	−0·44	−0·27	−0·23	+0·337	−0·763	−0·52	−0·15	+0·32	−0·78	+1·066
								$-0·04^{3+}$			$+0·52^{+}$						
(9549)	(2923)	(1591)	(1199)	(1031)	(977)	(723)	(1070)	(871)	(1001)	(984)	(1175)	(1616)	(1584)	(1110)	(1278)	(1707)	
Kr	Rb	Sr	Y	Zr^{4+}	Nb^{3+}	Mo^{3+}	Tc	Ru^{2+}	Rh	Pd	Ag	Cd	In^{2+}	Sn	Sb	Te	I
	−2·925	−2·89	−2·37	−1·53	−1·1	−0·2		+0·45	+0·6	+0·83	+0·799	−0·402	−0·342	−0·136	+0·18	−0·92	+0·536
(19209)	(3611)		(1743)	(1457)	(1339)	(941)		(933)	(1071)	(1391)	(1668)	(2197)	(2542)	(1769)	(1846)	(2079)	(5140)
Xe	Cs	Ba	La	Hf^{4+}	Ta	W^{6+}	Re	Os^{2+}	Ir	Pt	Au^{+}	Hg	Tl^{+}	Pb	Bi	Po	At
	−2·92	−2·92	−2·4	−1·7		−1·1	−0·252	+0·7	+1·0	+1·2	+1·7	+0·798	−0·335	−0·126	+0·28	+0·56	
											$+1·42^{3+}$						
(10609)	(4151)		(2502)	(1730)	(1610)	(1158)	(1344)	(845)	(1268)	(1594)	(1938)	(3185)	(2941)	(2973)	(2495)		
Rn	Fr	Ra	Ac	Th^{4+}	Pa	V^{6+}	Np	Pu^{3+}									
		−2·92		−2·1		−0·82	−1·86	−2·03									
						$-1·80^{2+}$											
(11069)				(2231)		(2057)		(2124)									

*Free energies are given in brackets to be preceded by a negative sign.

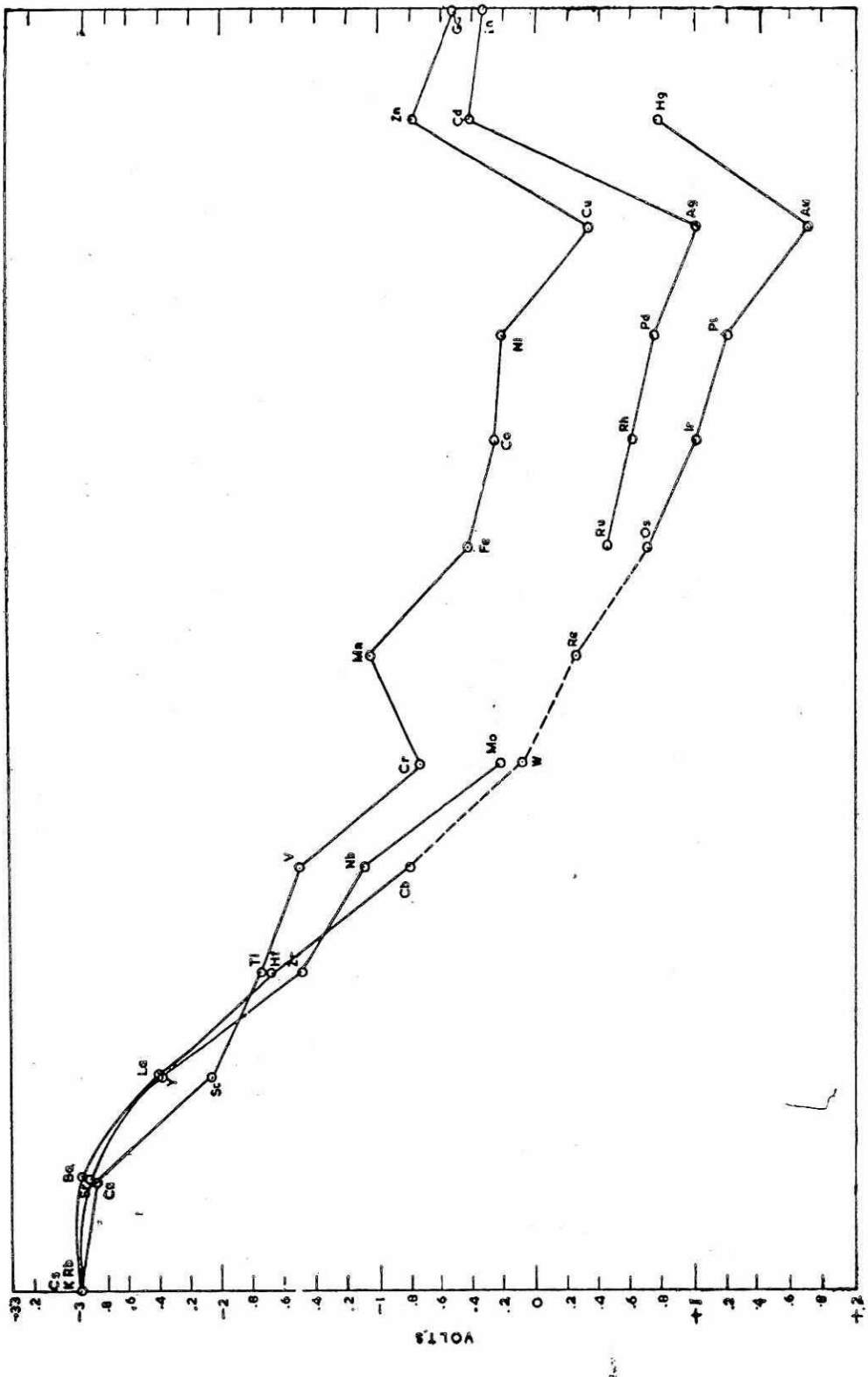

FIG. 2.VI — STANDARD ELECTRODE POTENTIAL VALUES OF THE ELEMENTS OF THE THREE LONG PERIODS

of alpha manganese containing selenium which explains the very high efficiencies obtained in the case of alpha deposition in presence of selenium to those obtained with sulphur.

Cathode potential — It has not been possible to electro-deposit pure alpha manganese directly to any appreciable thickness without the presence of sulphur or selenium in the electrolyte and so the cathode potential could only be measured for deposition of alpha manganese with sulphur or selenium.

From Table 2.III it is seen that the cathode potential for deposition increases in the following order:

1. Pure gamma manganese
2. Alpha manganese containing sulphur
3. Alpha manganese containing selenium

This order of sequence is in conformity with the order of standard potential values given in the earlier section.

Looking at the standard potential values, alpha manganese containing no sulphur or selenium should deposit at a lower cathode potential than gamma manganese. It can be seen[14] that a flash layer of amorphous manganese resembling alpha manganese is obtained from pure solutions over which gamma manganese begins to build up in absence of reducible sulphur or selenium compounds. This flash layer of amorphous manganese, as soon as it is formed, facilitates hydrogen discharge because of its very low hydrogen over-voltage. Discharge of the hydrogen ions makes the vicinity of the cathode more alkaline when the potential for evolution of hydrogen is raised up. Thus, when the potential rises up, gamma manganese begins to deposit which has a high hydrogen over-voltage.

If cathode potential were the only factor for alpha and gamma deposition, then at a lower potential alpha manganese should deposit, and at the higher cathode potential gamma manganese should deposit. But alpha manganese is obtained only in presence of reducible sulphur or selenium compounds in the electrolyte when the cathode potential values are raised. It is quite understandable that the presence of reducible compounds of sulphur or selenium can make the cathode potential more negative at a given current density due to its negative catalytic effect on the combination of hydrogen atoms to form molecules[15]. The negative catalytic effect on combination of hydrogen atoms on the cathode surface results in a high hydrogen over-voltage, selenium[16] having a far powerful negative effect.

Summing up, though pure alpha manganese should preferentially be deposited at a lower potential, it is obtained only when the potential

is raised up by the addition of sulphur or selenium compounds. Further it is seen that neither the standard potential nor the cathode potential values differ very much between the two modifications.

Hammerquist[17] has given the values of cathode potential during the deposition of manganese as

referred to saturated calomel as zero	−1·65
referred to hydrogen electrode as zero	−1·40

which, as seen from Table 2.III, agrees very well with the values obtained in this investigation. Hammerquist[17] continues to say that manganese will deposit initially on the cathode without the presence of sulphur dioxide but it will cease after the cathode is covered with manganese. According to him, manganese catalyses the evolution of hydrogen at lower than normal potentials and that the presence of sulphur dioxide acts either as a polarizing agent to polarize the cathode with respect to hydrogen or acts as a catalytic poison. As pointed out in the discussion of the electrode potential curves with time of various forms of manganese, pure alpha manganese has low hydrogen over-voltage as mentioned by Hammerquist above.

But it is found that presence of polarizing agents in the electrolyte other than sulphur, selenium or tellurium does not effect the deposition of manganese in alpha modification[14]. It is not only the polarizing action of sulphur group but also some other properties, probably the high hydrogen content of the deposit obtained in presence of sulphur group which effects the deposition of manganese in alpha modification[14], as can be seen in Chapters IV and V

Conclusion

The standard electrode potential of pure alpha manganese (containing no sulphur or selenium) is less negative than that of gamma manganese and that the values for the two phases differ only slightly, as would be expected from the thermo-chemical data of the two phases.

The standard electrode potentials of alpha manganese containing sulphur or selenium are more negative than those of pure alpha manganese (containing no sulphur or selenium) and gamma manganese.

Cathode potential values for deposition of manganese in various phases for the same current density increase in the following order:

1. Pure gamma manganese
2. Alpha manganese containing sulphur
3. Alpha manganese containing selenium

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